

Combustion Research Facility NEWS



Rotation of NO Recoiling from Argon Collision Depends on Deflection Angle

When a diatomic molecule is struck by an atom, it recoils from the collision spinning. The energy transfer process is fundamental to how gasses heat up, cool down, and come to equilibrium. David Chandler in collaboration with Dr. Joseph Cline, University of Nevada at Reno, has been studying this process in great detail. For each rotational state produced in a collision, Dave, Joe, and their colleagues have measured the angle at which the recoiling molecule scatters (known as the differential cross section), the alignment of the rotational angular momentum vector, and most recently the orientation of that angular momentum vector. This is the first time scientists have measured the rotational orientation or direction – clockwise or counterclockwise – of molecules after a full two-body collision. They found that not only is there a preferred sense of rotation, but that that sense of rotation depends on the rotational state of the diatomic molecule and the angle at which the molecule scatters.

In order to make this measurement, Dave and Joe combined crossed molecular beams, circularly polarized resonant multiphoton ion-beam probing, and velocity-mapped ion-imaging detection. This apparatus allowed them to measure the sense of rotation for each scattered molecule as a function of scattering angle and rotational state. They chose NO scattering from argon atoms to measure

this fundamental property for several reasons. First, NO is an easy molecule to monitor experimentally because of its low ionization potential and convenient and well-assigned spectroscopy. Second, it provides a good theoretical representation of the collision of a radical species with an atom. Third, although NO has an unpaired electron, and therefore requires inclusion of multiple potential energy surfaces to describe the dynamics, there are very detailed calculations on the NO +

argon systems available with which to compare the measured orientation. However, only the latest and most sophisticated of these calculations match the measured results.

After a collision with an argon atom, the NO molecules scatter off at many angles relative to the beam. Dave, Joe, and colleagues find that for any given scattering angle, the majority of molecules that spin off in that particular direction will be rotating the same way. For example, as is shown in Figure 1, at a scattering angle of 45 degrees approximately 80 percent of the molecules are spinning counterclockwise for a NO when the NO is scattered toward the top of the image and clockwise when scattered 45 degrees toward the bottom of the image. This pattern is different for each rotational state and is found to alternate at lower rotational states.

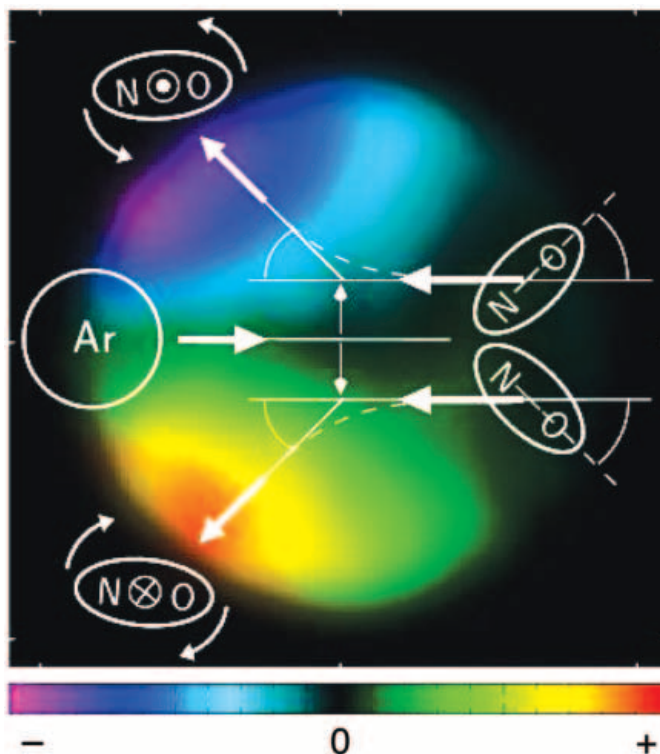


Figure 1. NO molecules scattered in collisions with argon show preferred senses of rotation (clockwise or counterclockwise) depending on their deflection angle. The false colored image above shows the orientation of the NO ($j=15.5$) resulting from NO scattered from argon with approximately 500 cm^{-1} of collision energy. Purple represents counterclockwise rotating molecules and orange represents clockwise rotation. These measurements were made on a crossed molecular beam apparatus with resonant enhanced multiphoton ionization (REMPI) probing and ion-imaging detection.

Isotopic Tracing by Accelerator Mass Spectrometry Shows Fate of Tagged Diesel Fuel Oxygenate

The origin, characterization, and fate of particulate matter in combustion reactions have long been subjects of study at the CRF. Pressure to significantly reduce particulate emissions from diesel engines has added a new urgency to research into understanding the chemical mechanisms of soot formation. An enhanced understanding of such mechanisms would enable the identification of fuel formulations that can minimize emissions while improving combustion.

Experiments carried out by Chuck Mueller and Glen Martin at the CRF, in collaboration with Bruce Buchholz at Lawrence Livermore National Laboratory (LLNL), have shown that isotope tracing with accelerator mass spectrometry (AMS) can be a potent tool for finding out how fuel formulation affects soot formation in diesel engines. They found that when dibutyl maleate (a proposed diesel-fuel oxygenate, see Figure 1) was tagged with carbon-14 (^{14}C) at the carbon-oxygen double bond, very little ^{14}C ended up in the soot.

While measurements of emissions of particulate matter, hydrocarbons, and CO are

routine, determining the origin of the carbon atoms that make up these exhaust products has proved difficult. Researchers in the mid-eighties labeled fuel components with large quantities of ^{14}C and traced the isotope to particulate matter from a diesel engine or diffusion flame using a decay-counting technique. These experiments required special radioactive test facilities. In contrast, the high sensitivity of AMS enables accurate measurements to be made using samples with ^{14}C concentrations so small that they are not considered radioactive, hence the hazards and expenses associated with a radioactive test facility are avoided. ^{14}C is naturally produced in the upper atmosphere and is present in living organisms at a level of 1.2 parts in 10^{12} . AMS is routinely used to measure concentrations that are only a fraction of this naturally occurring value.

Known since 1977 to be an extremely sensitive technique for measuring small concentrations of isotopes, AMS has been finding new applications in biomedicine, environmental monitoring, food science, and now combustion research. In AMS, a sample is converted into an ion beam,

which is passed through an accelerator and then through a sequence of mass, charge, and velocity filters that eliminate all but the particular isotope of interest. The research reported here melded the capabilities in the CRF's Alternative Fuels Optical Engine Laboratory with those of LLNL's Center for Accelerator Mass Spectrometry, now the most versatile and productive AMS facility in the world.

The addition of oxygenates to diesel fuel can reduce particulate emissions, but the underlying reasons for the reductions are not understood. Dibutyl maleate, spiked with several μl of dibutyl maleate that has been labeled with ^{14}C at the 1,4-maleate position (see Figure 1), was burned in the modified 350-hp Caterpillar optical engine. Soot was collected on filters, and the ^{14}C content measured by AMS. The almost complete lack of ^{14}C in the particulate matter suggests that the carbon-oxygen double bond does not break during combustion. Experiments designed to determine the fate of carbon labeled at the 2 and 3 maleate and the butyl carbon bonded to oxygen are presently underway.

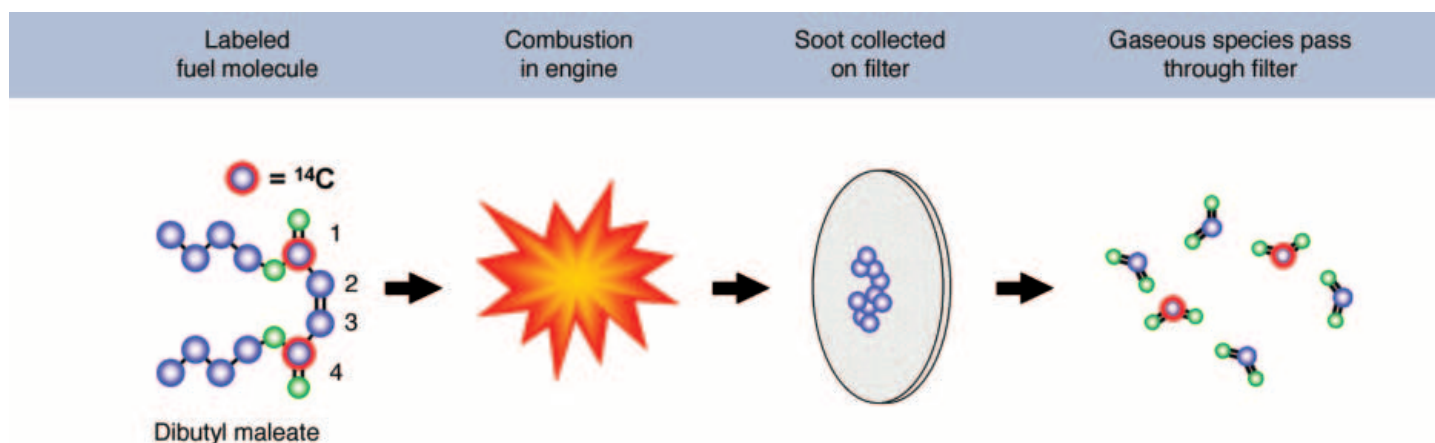
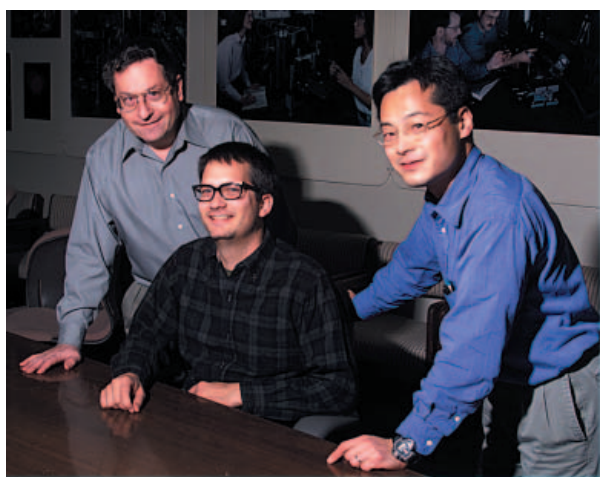


Figure 1. The fate of fuel-molecule carbon in combustion reactions can be determined by carbon-14 labeling the molecules at specific carbons and determining the isotope ratio in the combustion products by accelerator mass spectrometry. This schematic shows the positions of carbon-14 labels, combustion, and the separation of gaseous and solid combustion products. The experiments combined the capabilities of the Alternative Fuels Optical Engine Laboratory at the CRF and the Lawrence Livermore National Laboratory's Center for Accelerator Mass Spectrometry.



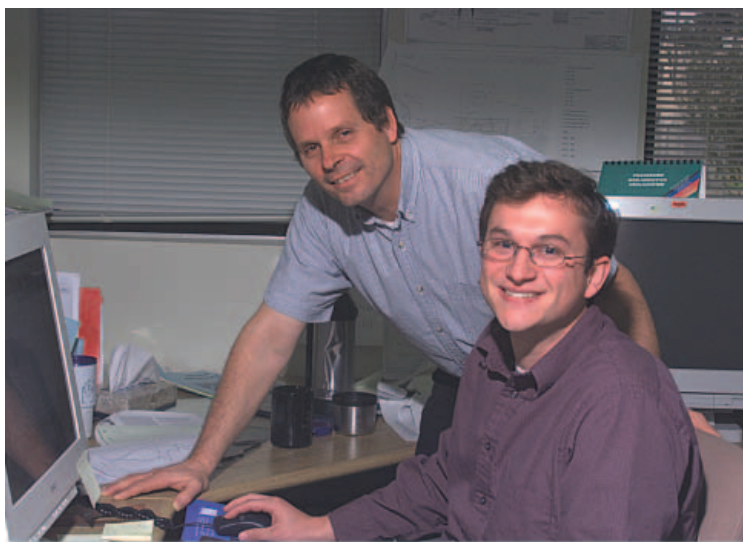
During a recent four-month visit, Sheila Gallagher (left) of the National University of Ireland (NUI) assisted Andy McIlroy (right) in measuring temperature profiles and OH concentrations by laser-induced fluorescence and cavity ringdown spectroscopy in low-pressure 1,3-butadiene flames. Sheila has returned to Ireland to finish her Ph.D. with Professor John Simmie of the NUI Chemistry Department.



Professor Josh Halpern (left) of Howard University visited the CRF from December 2001 through January, 2002, to work on cavity ring-down spectroscopy and vinyl radical kinetics with Craig Taatjes (center). Professor Atsumu Tezaki (right), University of Tokyo, recently completed a nine-month visit to Craig's laboratory, during which time he investigated DO_2 formation in deuterated alkyl + O_2 reactions.



Tarek Echekki (seated) recently joined the faculty of the Mechanical and Aerospace Engineering Department at North Carolina State University as an associate professor after completing postdoctoral and limited term appointments in the Reacting Flow Research Department at the CRF. During his tenure at Sandia, Tarek worked closely with Jackie Chen (left) on direct numerical simulations of turbulence-chemistry interactions in premixed and partially premixed hydrocarbon flames and on autoignition in inhomogeneous hydrogen-air mixtures. Working with Alan Kerstein (right), Tarek incorporated complex chemistry into a novel turbulence model that captures salient features of turbulent jet diffusion flames studied experimentally in the Turbulent Combustion Laboratory at the CRF.



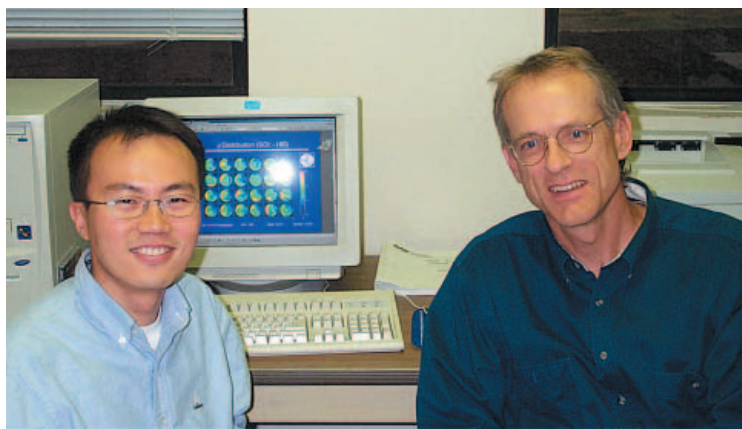
Marcus Megerle (seated), a visiting researcher from the University of Michigan, is working with Paul Miles to clarify the mechanisms of turbulence production in swirl-supported diesel engines. Their work has shown that the interaction of the fuel sprays with the swirling flow field can generate an unstable distribution of angular momentum, which significantly enhances flow turbulence (see CRF News, November/December 2001).



Sam Clegg, (left), a post-doctoral researcher with David Osborn, recently accepted a permanent position at the Air Force Research Laboratory at Kirtland Air Force Base in New Mexico. While Sam was at the CRF he studied photodissociation dynamics using time-resolved Fourier transform spectroscopy. In his new position Sam will be studying energy transfer processes relevant to the COIL (Chemical Oxygen Iodine Laser) system under development at Kirtland Air Force Base.

Researchers Launch SciDAC Terascale Simulations Project

The CRF recently hosted a kick-off meeting for the project "Terascale High-Fidelity Simulations of Turbulent Combustion with Detailed Chemistry" sponsored by the DOE's new initiative on Scientific Discovery Through Advanced Computing (SciDAC) in Computational Chemistry. The meeting was held at the CRF on October 28–29, 2001 and participants from a consortium of research institutions including University of Maryland, University of Michigan, University of Wisconsin, and the Pittsburgh Supercomputing Center attended the meeting. The objective of this new program is to develop a terascale high-fidelity direct-numerical simulation (DNS) software capability for the simulation of turbulent reactive flows, starting from an existing Sandia DNS code. The focus is on including extensive new physical modeling developments (soot, spray, and radiation models) along with complex geometry in an advanced software framework. Benchmark simulations will include turbulent autoignition in homogeneous charged compression ignition engines and pollutant formation in turbulent jet diffusion flames.



Donghee Han has been working with Richard Steeper in the gasoline direct-injection laboratory examining the evaporative behavior of fuel/tracer mixtures used for in-cylinder, laser-induced fluorescence measurements of equivalence ratio (see CRF News this issue, page 5). Donghee has recently taken a position at Hyundai Motor Co. in Korea.

The CRF News is published bimonthly by the Combustion Research Facility, Sandia National Laboratories, Livermore, California, 94551-0969.

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Experiments Target Improved Fluorescent Tracers for Equivalence-Ratio Imaging in Internal Combustion Engines

Understanding the fuel/air mixture preparation process is essential for the design and operation of internal combustion engines, especially for advanced engine designs such as spark-ignition direct-injection (SIDI) and homogeneous-charge compression-ignition (HCCI) engines. An important tool used to study in-cylinder fuel/air mixing is laser-induced fluorescence (LIF) imaging. This laser diagnostic tool typically relies on a mixture of non-fluorescing fuel doped with a small amount of fluorescent tracer. In order to properly track the fuel component, the tracer must co-evaporate with the fuel. Donghee Han and Richard Steeper have recently completed an experimental examination of the required evaporative characteristics of such fuel/tracer mixtures, highlighting weaknesses of commonly used mixtures and proposing improvements.

Commonly, fuel/tracer mixtures are formulated with a single alkane fuel plus 5–10% of a ketone or aromatic tracer. By selecting a fuel and tracer with similar boiling points and heats of vaporization, such as isooctane and 3-pentanone, it is commonly and erroneously assumed that the liquid components will necessarily co-evaporate. But this assumption ignores the possibility of molecular interactions in solution that can lead to preferential evaporation of one of the components.

To investigate the evaporation behavior of fuel/tracer mixtures, the Sandia researchers recorded the vapor-phase LIF of evaporating solutions in a bench-top experiment. Figure 1 shows the LIF signal histories of three isooctane/ketone mixtures. The x-axis

represents the experiment progress variable, with liquid mass normalized to 1 at time zero (time proceeds from right to left as the mass of liquid decreases). The red data

indicating that the 3-pentanone is more volatile than isooctane in this mixture. The rising green data indicate that the next heavier ketone (3-hexanone) is less volatile than isooctane at these same proportions. Because the ketone tracers in these two mixtures do not co-evaporate with the isooctane, neither can properly track the vaporizing fuel, and LIF equivalence ratio measurements using such mixtures would be inaccurate.

But the mirror-image trends of the two binary mixtures in Figure 1 suggest the possibility of combining both tracers to achieve the desired constant-LIF signal. A series of tests uncovered the promising mixture of isooctane plus 9% 3-hexanone and 1% 3-pentanone, yielding the LIF data shown in magenta in Figure 1. The fact that this LIF signal remains close to unity during most of the experiment indicates that the tracer combination co-evaporates with isooctane, and as such should track the fuel vapor during engine experiments, achieving an improvement in equivalence ratio measurement accuracy.

Success in matching the evaporation of an alkane fuel with multiple tracers led to the application of the technique to a fuel/tracer mixture containing two alkanes of unequal volatility. The motivation for such work is the desire to make equivalence ratio measurements of a more realistic, multicomponent fuel. With two main fuel components, the total evaporation rate is no longer flat, as illustrated by the green data in Figure 2. These data show a declining evaporation rate as the concentration of the high-volatility fuel (cyclopentane) is rapidly depleted. In this case, tracer proportions must be adjusted so that the LIF signal tracks the instantaneous evaporation rate. If this is accomplished, then each incremental mass of liquid evaporated will produce the

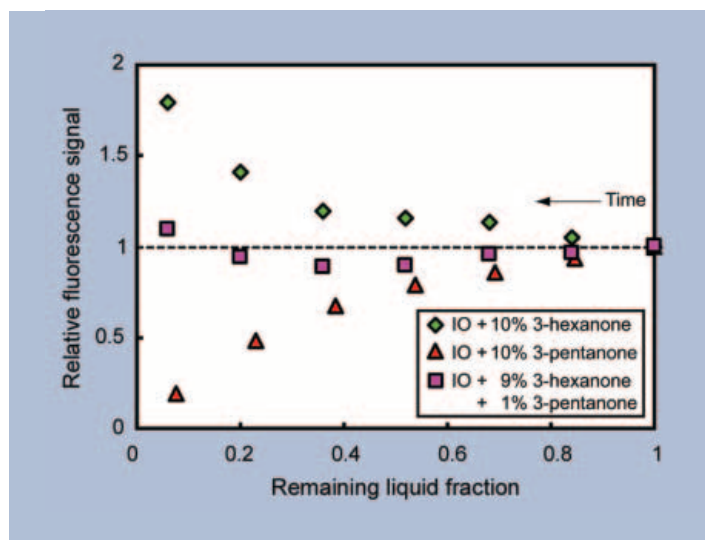


Figure 1. Relative vapor-phase LIF history during the evaporation of two binary mixtures (fuel plus tracer) and one ternary mixture (fuel plus two tracers). Initial compositions (by volume) are indicated in the legend.

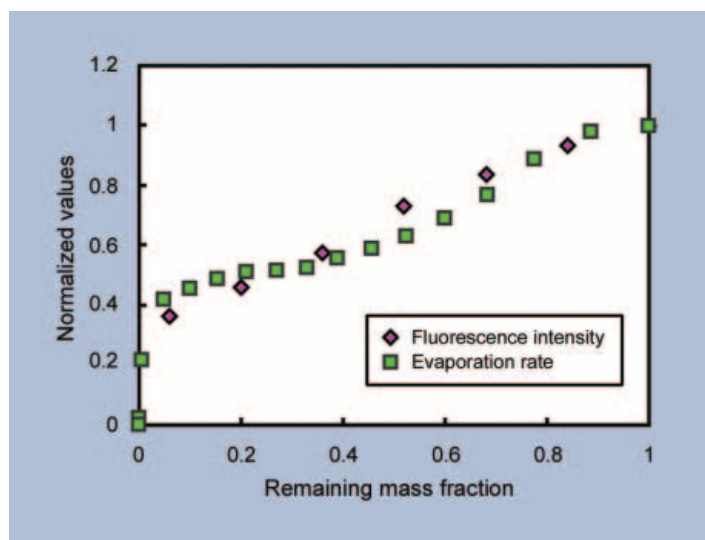


Figure 2. Instantaneous mass evaporation rate and LIF intensity recorded during the evaporation of a mixture of 70% isooctane, 20% cyclopentane, 4.5% 3-hexanone, 4% 3-pentanone, and 1.5% 2-butanone.

points correspond to a mixture of 10% by volume pentanone in isooctane. The total mass evaporation rate of the mixture is relatively constant (not shown), but the LIF data reveal that the tracer concentration drops dramatically during the experiment,

same incremental LIF signal intensity. The magenta data points in Figure 2 correspond to a mixture of the two fuels plus three tracers, and illustrate that the desired tracking has been achieved.

Selected multicomponent fuel/tracer mixtures from the above study were tested in a fired, direct-injected gasoline engine. The optically accessible engine allowed the capture of planar LIF images in the vicinity of the spark plugs near the time of ignition. The images were converted to two-dimensional equivalence ratio maps, from which probability density functions (PDF) were obtained to help visualize the in-cylinder fuel/air mixing process. Figure 3 presents PDFs for two mixtures. The PDF labeled two-alkane corresponds to the two-fuel, three-tracer mixture shown in Figure 2. The second mixture (labeled single-alkane) contains a single fuel component (cyclohexane) mixed with the tracer 3-pentanone at proper proportions for co-evaporation.

The data in Figure 3 represent injection at bottom center of the intake stroke –

late enough that mixing is not complete by the time of image capture. As a result, the PDFs for both fuel/tracer mixtures show a wide distribution of equivalence ratios. But the fact that the two-alkane PDF is wider than the other indicates that in-cylinder mixing is less complete for this fuel/tracer mixture. The average fuel volatility was selected to be about the same for the two mixtures. Therefore, the slower fuel/air mixing for the two-alkane case may be interpreted to mean that evaporation and subsequent fuel/air mixing are controlled by the least volatile fuel component.

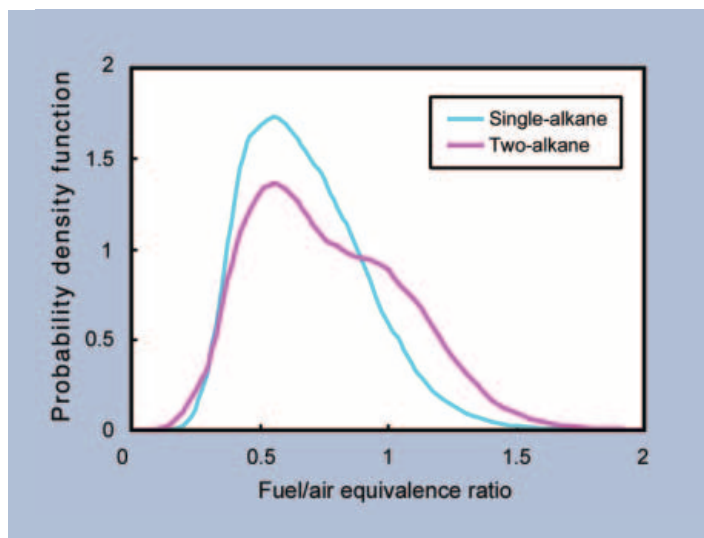


Figure 3. Probability density of in-cylinder equivalence ratio recorded close to the time of ignition for two mixtures: 70% isooctane, 20% cyclopentane, 4.5% 3-hexanone, 4% 3-pentanone, and 1.5% 2-butanone (two-alkane mixture); and 90% cyclohexane, 10% 3-pentanone (single-alkane mixture).

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000

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